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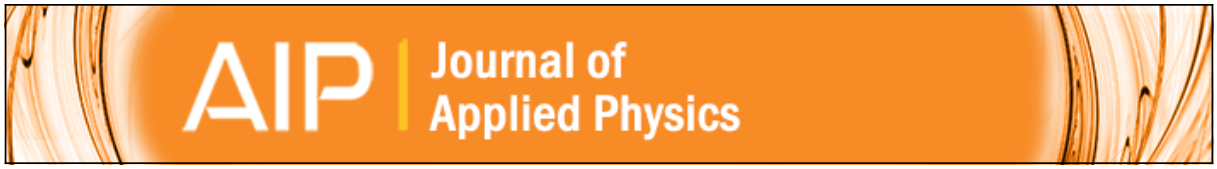

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First-principles study of Cl diffusion in cubic SiC

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Chlorine-based precursors allow the fast growth of thick SiC epilayers for fabricating high-voltage devices. Since it was demonstrated that epitaxial growth with a Cl-based chemistry can affect *p*-type doping, the issue of Cl diffusion SiC is technologically relevant therefore we present a first principles study of the migration mechanisms of Cl in cubic SiC. We first discuss the equilibrium structure of different Cl-related defect configurations (isolated interstitials and complex defects) which have either been reported in the literature or calculated in the present study. Following this analysis, we focus on two migration mechanisms: The interstitialcy and the vacancy-mediated mechanism. We found that Cl diffuses in SiC via a vacancy-mediated mechanism and the value of the diffusivity is estimated. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4799194]

I. INTRODUCTION

In order to favor a more widespread use of SiC for mainstream applications, e.g., consumer electronics, the SiC industry has to supply affordable material of very high crystalline quality. The typical growth rates of SiC, employed in chemical vapor deposition (CVD), do not exceed $5-15\,\mu m/h$ because high flow rates result in the formation of Si droplets.[1] These, by coming into contact with the crystal surface, give rise to macro-defects in the epilayers and, as a result, the growth of thick epitaxial layers becomes lengthy and costly. A solution to this crucial issue was proposed several years ago by La Via *et al.*[1] who showed that chlorinated precursors allow an increase of growth rates, paving the way to the fast growth of good quality thick epilayers.[2] The introduction of Cl in the reactor in the form of HCl, $CH_x\ Cl_y$, $SiH_x\ Cl_y$, prevents the formation of the above mentioned droplets because Cl can bind to Si, by forming either $SiCl_y$ or $SiH_x\ Cl_y$ that do not polymerize at typical growth temperatures and can be flushed away from the growth chamber. As a result, Si aggregates are absent and this allows the increase of the flow rate and, consequently, of the growth rates. If on one side, the use of Cl-based precursors is beneficial for increasing growth rates, on the other side, studies have shown that Cl incorporation in SiC epilayers may be possible,[3,4] raising the question of the effects of Cl impurities on the electronic properties of SiC.

La Via *et al.*[1] have shown, by deep level transient spectroscopy (DLTS), that both the $Z_{1/2}$ and $EH_{6/7}$ levels are present in *n*-type 4H-SiC, grown by using HCl as a precursor, and that Cl-related deep levels are not observed, at least in the $10^{13}\ cm^{-3}$ range. To the contrary, a recent DLTS study performed on Cl-implanted 4 H-SiC epilayers[5] has shown that the involvement of Cl in the microscopic structure of defects detected in either *n*- or *p*-type SiC is feasible. While a conclusive experimental evidence for the existence of Cl-related defects is still needed, theoretical studies have predicted that substitutional Cl at a C-site, and Cl-related complexes, with either the silicon vacancy (V_{Si}) or Al, are donors.[6,7] The donor character of Cl and related complexes can explain why chlorinated precursors do not affect the net-donor concentration[8] but can affect the net-acceptor concentration[9,10] of Cl-grown 4H-SiC epilayers. In addition, whether or not Cl, introduced either during growth or by $POCl_3$ annealing,[11] can diffuse and affect the electronic properties of SiC is still an open question. Despite the technological relevance of the issue, the mechanism of Cl migration is still unknown and, for this reason, we present a first-principles study on Cl diffusion in cubic SiC. After analyzing the equilibrium structures and formation energies of several Cl-related defects, two possible diffusion mechanisms (interstitialcy and vacancy mediated) are discussed and the Cl diffusivity coefficient is estimated.

II. COMPUTATIONAL METHOD

We employed spin-polarized density functional calculations to calculate the equilibrium configurations and formation energies E_{form} of Cl-related defects in a 64-atom cubic SiC supercell. Calculations were carried out using the siesta package,[12] in the local density approximation (LDA) with the exchange correlation functional of Ceperley and Alder[13] and norm-conserving Troullier-Martins pseudopotentials[14] and a double-ζ plus polarization atomic orbitals basis set. Additional details and convergence tests can be found in Refs. 6 and 7. The formation energy E_{form} of five Cl-related defects was calculated by using the formalism of Northrup *et al.*[15] (see also Eq. (17) of Ref. 16), in the stochiometric limit, and by including the Madelung correction. The defects considered in this study are: Cl in hexagonal position (Cl_{Hex}), that is equidistant from three C and three Si atoms, the $\langle 110\rangle$ ($Cl_{spC\langle 110\rangle}$) and $\langle 100\rangle$ ($Cl_{spC\langle 100\rangle}$) Cl-split interstitials. Since Cl favors a C-site,[5] we also considered the Cl_C complex with C in either tetrahedral ($Cl_C - C_{Td}$) or hexagonal ($Cl_C - C_{Hex}$) interstitial positions.

In order to investigate the migration of Cl, that is finding the saddle point geometry, we employed the constrained relaxation scheme by Kaukonen *et al.*,[17] that has been successfully used in other diffusion studies in SiC.[18–20] In this method, the initial (*A*) and final (*B*) structures, both fully

relaxed, are known. The diffusing specie is then moved in small steps from A to B and allowed to relax in a plane perpendicular to the AB direction. By plotting the total energy (E_{tot}) of the system after each step, the migration energy (E_{mig}) of the diffusing specie is obtained as the energy difference between the minimum energy and the saddle point structures. The constrained relaxation scheme is also applied to the case of a two-atom coordinated motion, e.g., concerted exchange mechanism.[20] The motion of the two atoms is considered as the rotation of the dimer which, by constraining one angle α, it is free to rotate around the other angle β, to stretch and to rigidly translate. By varying α between 0 and π, we plotted the E_{tot} of the system versus the rotational space and obtained E_{mig} in a similar fashion to the one-atom case.

In this work, we investigated the diffusion process at 1570 °C (typical growth temperature)[3] and for this reason, we followed the procedure described by Rauls *et al.*[18] Unlikely the case of calculations performed at T = 0 K, at T > 0 the E_{form} has to be estimated by considering the Gibbs free energy (G)

$$G = E_{tot} + U_{vib} - TS + pV, \tag{1}$$

where U_{vib} is the vibrational energy, S is the entropy, p is the pressure, and V is the volume of the system. In fact, if we neglect the last term, at T > 0, the contribution of both U_{vib} and S must be kept into account by performing a calculation of the phonon modes, by the force constant method,[12] for all minimum energy structures as well as saddle point geometries. Once the vibrational frequencies ω_i are calculated (at the Γ point), assuming a constant volume with N, k_B is the number of particles and the Boltzmann constant, respectively, both U_{vib} and S are estimated by

$$U_{vib} = \sum_{i=1}^{3N} \left(\frac{\hbar\omega_i}{e^{\hbar\omega_i/k_BT}} + \frac{1}{2}\hbar\omega_i \right), \tag{2}$$

$$S = k_B \sum_{i=1}^{3N} \left[\frac{\hbar\omega_i}{k_BT} (e^{\hbar\omega_i/k_BT} - 1)^{-1} - ln(1 - e^{-\hbar\omega_i/k_BT}) \right], \tag{3}$$

and finally included in G.

Once the mechanism for migration is found and the entropy is calculated for both minimum energy and saddle point geometry, the activation energy for diffusion (E_{act}) is calculated as the sum of E_{form} and E_{mig}. From E_{act}, the diffusivity, D, is obtained from $D = D_o e^{-E_{act}/k_BT}$ with D_o the diffusion coefficient $D_o = \frac{d^2 c_o p}{2} e^{\Delta S/k_B}$, with d, c_o, p, ΔS, the distance between the initial (at point A) and final (at point B) structures, the frequency factor (1.6×10^{13} s^{-1}), the vacancy concentration divided by the number of sites in the sublattice and the entropy difference between the ground state and the saddle point, respectively.

III. RESULTS AND DISCUSSION

A. Formation energies

It is now well-established that, among SiC impurities, B and Al migrate via a kick-out mechanism[19,21,22] while N, P, and O favor an interstitialcy mechanism.[22,23] Since the diffusion of substitutional impurities, like Cl, can occur either via interstitials or vacancies, we assume that one of these two mechanisms may also apply to the migration of Cl. In order to investigate an interstitial-mediated diffusion, we have examined several possible configurations of the isolated Cl impurity in interstitial positions, that is in hexagonal (Cl_{Hex}, equidistant from three C and three Si atoms) and split interstitial ($Cl_{spC\langle 110\rangle}$, $Cl_{spC\langle 100\rangle}$) position and two substitutional-Cl related complexes with a C interstitial ($Cl_C - C_{Td}$, $Cl_C - C_{Hex}$). Tetrahedrally carbon/silicon coordinated Cl interstitials have been investigated elsewhere.[6]

As Fig. 1 shows, the lowest E_{form} is that of the Cl_{Hex} and $Cl_{spC\langle 110\rangle}$ for all values of E_F. This can be explained in terms of geometry relaxation: Unlikely Cl at a C-substitutional site, Cl in the interstitial position is not energetically stable,[6] for this reason when Cl occupies an interstitial site, it will preferably move to the more energetically stable C-site. In fact, after geometry relaxation, the three C and three Si atoms surrounding Cl_{Hex} move 0.20 Å away from Cl which, in a second time, moves toward one of the neighboring C atoms, pushing it 0.51 Å off its site. In this way, both Cl and C are found at a distance of 1.68 Å from each other and occupy the same C-site on the $\langle 110\rangle$ direction. This new defect configuration is the same resulting from the relaxation of $Cl_{spC\langle 110\rangle}$, that is a Cl and a C, sharing a C-site, with a bond length of 1.68 Å.

At a higher E_{form}, the $Cl_C - C_{hex}$ complex can be found. When relaxing a Cl atom in a substitutional position (Cl_C) and a C atom in hexagonal position, the C atom moves away from the hexagonal site, toward the Cl atom. Unlike the case of the isolated Cl_{hex}, the Cl–C bond is longer (2.23 Å) and the C atom binds also to another C atom. The presence of a C_{hex} and that of the new C–C bond raises the E_{form} because C_{hex} and C-aggregates generally have high E_{form}, ranging from 6 to 8 eV (Ref. 21) and 6.4 to 8.5 eV,[24] respectively.

By replacing C in the hexagonal position with a tetrahedrally coordinated C atom ($Cl_C - C_{Td}$), the E_{form} becomes ~12 eV, the same of that of a $Cl_{spC\langle 100\rangle}$. The result of the geometry relaxation of $Cl_C - C_{Td}$ is similar to that of $Cl_{spC\langle 100\rangle}$. In fact, for $Cl_C - C_{Td}$, the C atom moves toward the Cl atom, pushing it off the C-site giving rise to a Cl–C

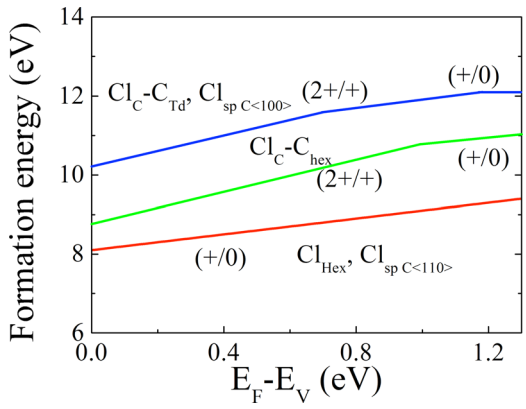

FIG. 1. Formation energies, shown in the underestimated LDA band gap, of an isolated interstitial (Cl_{hex}), two split interstitials ($Cl_{spC\langle 100\rangle}$, $Cl_{spC\langle 110\rangle}$), and two C-related complexes ($Cl_C - C_{Td}$, $Cl_C - C_{hex}$) in cubic SiC.

bond (∼2.4 Å) and ending in a configuration similar to that of $Cl_{spC\langle 100\rangle}$.

B. Migration mechanisms

The transformation of an isolated Cl_{Hex}, into a ⟨110⟩ Cl-split configuration, suggests that the migration of Cl is likely to be dominated by an interstitialcy mechanism rather than a direct interstitial migration therefore we consider the migration path (*AB*), between two relaxed $Cl_{spC\langle 110\rangle}$ configurations. In Fig. 2, the minimum energy profile for the diffusion of the singly positive charged $Cl_{spC\langle 110\rangle}$, via the interstitialcy mechanism, is presented. In addition, the snapshots of Cl in four configurations: (i) initial (A), two intermediate steps (ii) and (iii), and the final (B) position (iv), are also shown. The minimum energy configuration of $Cl_{spC\langle 110\rangle}$ (i), corresponds to a Cl and a C slightly off a C-site with a Cl–C bond length of 1.68 Å and surrounded by three Si atoms (one at 2.0 and two at 2.4 Å). After the first two steps, the Cl atom remains at the same distance from the C atom and the relative energy has a slight increase due to the formation of a new bond with a fourth Si atom. However, the third step (ii) coincides with the highest distorted structure as Cl moves in a site which is equidistant from four Si-atoms (∼2.1 Å) and 1.9 Å away from a C atom, leading to an increment of the relative energy that corresponds to E_{mig} barrier of 4.3 eV. As diffusion proceeds further, the distance between Cl and the neighboring C-atom decreases so that the Cl–C bond length of 1.68 Å is restored while the four Si atoms remain roughly equidistant from Cl (2.0–2.5 Å). However, the system reaches a relative maximum at the sixth step (iii), when another C atom binds to Cl (2.0 Å) raising the relative energy. At the final step (iv), the structure and energy coincide with that of the initial (i) step.

By adding the contributions of the vibrational spectra of both minimum energy structure and saddle point geometry, the E_{mig} lowers 2.1 eV. From this value, we calculated the E_{act} and, since at 1570 °C the E_F is in the middle of the Kohn-Sham band gap, the E_{form} of $Cl_{spC\langle 110\rangle}$ was calculated to be ∼8.7 eV (Fig. 1). This corresponds to an E_{act} for the interstitialcy-mediated mechanism of 10.8 eV.

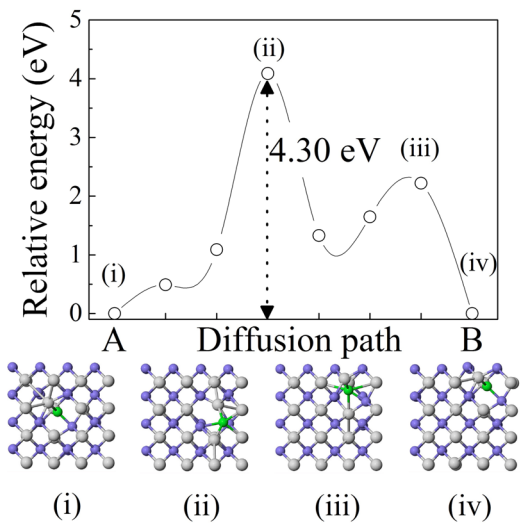

FIG. 2. Minimum energy path of the diffusion of a singly positive charged $Cl_{spC\langle 110\rangle}$ in cubic SiC. Four snapshots representing the configuration of the impurity with its nearest-neighbors, are also included. Silicon atoms are white, carbon atoms are blue, and chlorine is green. The solid line is meant as a guide for the eye.

Next, we turn to the analysis of a vacancy-mediated diffusion, by considering the $Cl_C V_{Si}$ complex[7] and using the dimer constrained relaxation procedure described in detail by Rurali *et al.*[20] A vacancy-mediated diffusion can occur via a ring mechanism by nearest neighbors' hops but this may lead to the formation of the $Cl_{Si}V_C$ complex, which should be unlikely since Cl is not stable at a Si-site. Instead, Cl diffusion can proceed by either concerted exchange of Cl and a C neighbor of V_{Si} (Fig. 3(a)) or by second-neighbor hop (Fig. 3(b)). As previously reported,[7] the triply, doubly, singly, and neutral charge states of $Cl_C V_{Si}$ are dominant for $E_F - E_V < 0.35$ eV, $0.35 < E_F - E_V < 0.6$ eV, $0.6 < E_F - E_V < 0.8$ eV, $E_F - E_V > 0.8$ eV, respectively.

In Fig. 4(a), the E_{mig} of the concerted-exchange for the neutral and the three charge states is shown. For a constrained angle of 45°, E_{mig} for all charge states is rather similar, ranging from 5.2 (neutral charge state) to 5.4 eV (triply charge state) which becomes 3.2 and 3.4 eV, respectively, after including the contribution of the vibrational energy. The similarity of these energy barriers can be explained by geometry relaxation because in both neutral and (2+/3+) charge state, the Cl atom ends up tetrahedrally surrounded by four Si atoms, with a bond length ranging between 2.3 and 2.4 Å. For a constrained angle of 90°, both the Cl atom and a second-neighbor C-atom move toward the empty Si site, in a configuration that resembles a split-interstitial, with a bond length of 1.68 Å, suggesting that, similarly to P,[25] also Cl split interstitials may form at either a C or a Si-site. The energy difference between the neutral and the (2+/3+) charge states may be due to the number of Si atoms to which Cl binds: In the neutral charge state, Cl is bonded to three Si atoms (∼2.6 Å) while for (2+/3+) Cl moves away from one of the surrounding Si atoms and remains bound to the other two.

In Fig. 4(b), we show the relative energy for the second-neighbor hop. For all migration steps, the Cl atom is surrounded by three Si atoms but the bond length changes leading to an increase and a decrease of E_{mig}. After the first migration step, Cl gets closer to one of the Si first neighbors (∼2.1 Å) and farther from the other two (∼2.4 Å) while the third step coincides with the lowest Cl-Si bond length (∼2.0–2.1 Å). This corresponds to an E_{mig} for the neutral and triply charge state of 6.5 eV (5.1 eV by including the vibrational energy) and 7.2 eV (5.8 eV), respectively. The Cl-Si

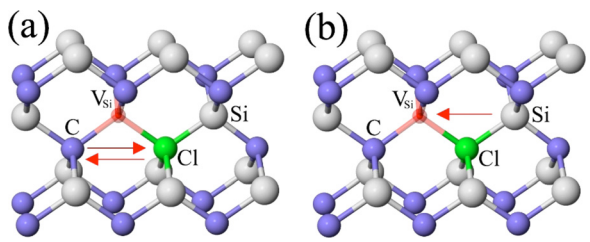

FIG. 3. Vacancy-assisted migration Cl via (a) concerted exchange of Cl_C and C and (b) site change of V_{Si} by second neighbor hop of a Si atom.

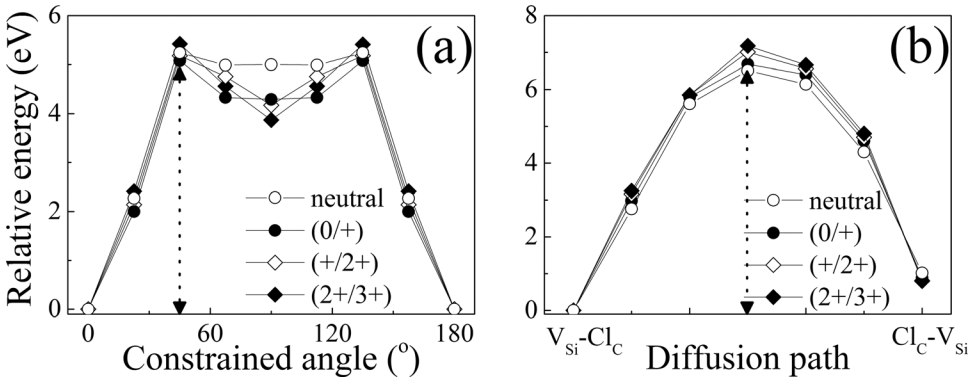

FIG. 4. Minimum energy path for (a) concerted exchange of Cl_C and C and (b) site change of V_{Si} by second neighbor hop of a Si atom, for the neutral, singly, doubly, and triply positive charge states of the Cl_CV_{Si} complex.

bonds start to stretch as migration proceeds further ~2.2–2.4 Å thus lowering E_{mig}.

As it can be seen, the lowest E_{mig} is achieved by a concerted exchange mechanism (Fig. 3(a)) and, by including the E_{form} of Cl_CV_{Si} for the case of the E_F level, calculated at 1570 °C, we obtain an E_{act} of 10.1 eV.

C. Discussion

The calculation of the E_{act} shows that Cl diffusion occurs via a vacancy-mediated mechanism (concerted exchange), rather than via interstitials, meaning that Cl may easily diffuse when large concentration of vacancies are present, e.g., in implanted or irradiated material. This would be the same as for silicon because Cl diffusion was found to be favored by the presence of vacancies after neutron irradiation.[26] If we calculate the diffusivity of Cl in SiC at 1570 °C, when a large concentration of vacancies ($\sim 10^{21}$ cm^{-3}, Ref. 18) is present, e.g., after ion implantation, the diffusivity becomes 2×10^{-17} cm^2/s. As a consequence, the presence of vacancies can trigger the diffusion of Cl which may end up bound to either doping impurities or vacancies, e.g., Cl_CAl_{Si}, Cl_CV_{Si}.

It can be thought that such mechanism may have occurred in Cl-implanted and annealed 4H-SiC epitaxial layers.[5] However, the concentration of vacancies ($\sim 10^{17}$ cm^{-3}) was such that, for annealing temperatures below 1700 °C, the diffusivity would be in the 10^{-20} cm^2/s range, yielding modest Cl diffusion. Only for higher annealing temperatures, Cl atoms become more mobile and an estimate of the diffusivity at 1800 °C yields $\sim 10^{-18}$ cm^2/s, suggesting that for T $\geq$ 1800 °C, Cl may diffuse and possibly give rise to electrically active complexes. Interestingly, after heat treatments at 1800 °C two levels, labelled *Ci*4 and *Ci*5, were found in n-type 4H-SiC.[5]

A high concentration of vacancies can also be found in the source/drain regions of a MOSFET, created by multiple ion-implantations. If Cl-based CVD epitaxial layers are used for the manufacture of such device, the vacancy-assisted diffusion of Cl impurities (that can be present up to 10^{14} cm^{-3}, Ref. 3) in the source/drain regions can be triggered by post-implantation annealing (1800 °C). As a consequence, the formation of Cl-related electrically active defects may lead to an increase of the density of states in the upper half of the band gap for *n*-type SiC. The question of Cl diffusion can also arise in the case of post-oxidation annealing (POA) processes that involve the use of Cl based gases, such as $POCl_3$. Although the behavior of Cl in SiO_2 has not been investigated yet, we believe that Cl should not harm the electronic properties of SiC because, provided that Cl atoms can diffuse through the oxide, the annealing temperature is around 950–1000 °C (Ref. 11) making Cl diffusion in SiC unlikely.

IV. CONCLUSIONS

The diffusion of Cl in cubic SiC was investigated by density functional theory. It was found that, after incorporation, Cl migrates via a vacancy assisted mechanism and the activation energy for diffusion is 10.1 eV at 1570 °C. After implantation, if a large concentration of vacancies is present, this activation energy corresponds to a diffusivity of 2×10^{-17} cm^2/s. In addition, heat treatments above 1700 °C, e.g., post implantation annealing of a MOSFET, can further enhance Cl diffusion giving rise to Cl-related complexes and increasing the density of states close to the conduction band in *n*-type epilayers.

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